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Final Report for AOARD Grant FA2386-13-1-4110
“Novel Catalyst for the Chirality Selective Synthesis of Single Walled Carbon Nanotubes”

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Abstract: Single walled carbon nanotubes (SWCNTs) are hollow carbon cylinders rolled up by a graphene sheet. Depending on the rolling direction of the graphene sheet, SWCNTs have different chirality, which lead to unique electronic and optical properties. Common synthesis methods result in SWCNTs with diverse structures. This structure-property diversity is a major hurdle in their applications. The aim of this project is to develop better fundamental understandings of chirality selective catalysts to achieve improved and tunable chirality control in SWCNT synthesis. In this two year project, remote plasma enhanced chemical vapor deposition was first used to manipulate carbon radical generation in carbon precursors. Using water assisted ethanol pyrolysis; how the water influences the yield and diameter of SWCNTs is revealed. It has also been found that introducing sulfur-containing compounds into carbon precursors can efficiently alter the chiral selectivity of a Co/SiO₂ catalyst toward different chiral SWCNTs. Next, a model catalyst based on CoSO₄/SiO₂ was developed, which shows good selectivity towards (9,8) nanotubes. Its selectivity can be tuned by catalyst calcination conditions, which affect the structure of sulfur near metal catalytic particles. Sulfur can be doped into Co/SiO₂ catalysts to change their chirality selectivity. Further, enrichment of (9,8) nanotubes was carried out by extraction using fluorene based polymers or an aqueous two-phase separation method. Highly enriched semiconducting (9,8) nanotubes were obtained for electronic transistor applications. Last, hybrid fibers were assembled in a linear hydrothermal microreactor using SWCNTs and graphene oxide sheets. Fiber micro-supercapacitors based on these hybrid fibers show great potentials for wearable electronics. Overall, this project demonstrates a clear path: SWCNTs of specific chirality can be grown in bulk using chirality selective catalysts, further enriched in solution, and applied to various novel applications.

Introduction: Single walled carbon nanotubes (SWCNTs) are hollow carbon cylinders rolled up from one layer of graphene sheet. Depending on the rolling direction of the graphene sheet, SWCNTs have different chirality, which lead to unique electronic and optical properties. They are potential candidate materials for the controlled propagation of electromagnetic energy because they can emit and detect electromagnetic energy in narrow wavelength windows. However, SWCNTs synthesized from all existing methods have a wide distribution of diameter and chirality. This structure-property diversity is a major hurdle in their applications. In the prevailing synthesis method (catalytic chemical vapor deposition), gaseous carbon precursor is catalytically converted into a solid nanotube at the surface of reactive catalysts. Previous experimental studies show that high-chiral-angle small diameter SWCNTs, such as (6,5) of 0.76 nm, can be obtained using chiral selective catalysts. However, the origin of this selectivity is unclear. Three major theories have been proposed: (1) the chiral selectivity is set during the

nucleation of chiral carbon caps on catalyst surface; (2) the growth rate of nanotubes is chirality-dependent; and (3) the growth termination or the lifetime of nanotubes depends on their chiral structures. For all these theories, experimental evidences are still missing providing a solid answer. It is fundamentally intriguing to better understand the chirality selectivity in SWCNT growth for developing novel methods to tailor the selectivity toward other chiral nanotubes. In our early study, we found that a Co incorporated mesoporous TUD-1 (Co-TUD-1) catalyst is selective to large-diameter (9,8) nanotubes ($d = 1.17$ nm) (*J. Am. Chem. Soc.*, 2010, 132, 16747). Elucidating the chirality selectivity mechanism towards (9,8) nanotubes will be very useful in designing new catalysts for improved SWCNT chirality control. The aim of this project is to develop better fundamental understandings of chirality selective catalysts to achieve improved and tunable chirality control in SWCNT synthesis. Our specific tasks are to understand what are the key components contributing to the chirality selectivity of Co-TUD-1 and what are their roles and how can we control them?

Experiment: Figure 1 illustrates major experiments carried out under the support of this project in the last two years.

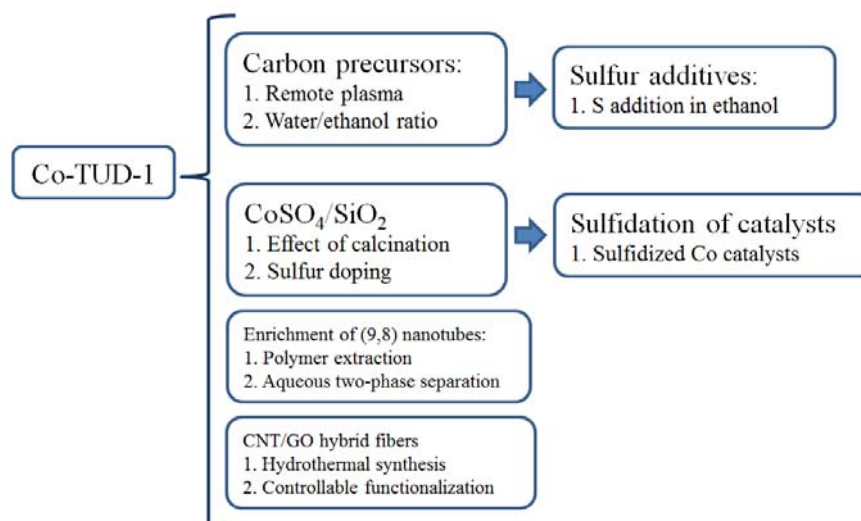


Figure 1. Overview of experiments carried out in this project

- (1) Our previous experimental (*J. Am. Chem. Soc.*, 2007, 129, 9014) and theoretical studies (*ACS Nano*, 2010, 4, 939) suggest that the chirality selectivity in SWCNT growth can be affected by different carbon radicals generated in chemical vapor deposition. Other researchers also reported that water can increase the yield and purity of SWCNTs. In this project, we further studied the effect of different carbon precursors and water on the chirality selectivity. First, we built a remote plasma enhanced chemical vapor deposition reactor, where remote plasma enables the decomposition of carbon precursors to occur away from the site of SWCNT growth. This allows separate manipulation of carbon radical generation and SWCNT growth. A series of syntheses were carried out at different plasma power and growth temperature to understand the effects of plasma power and growth temperature on chirality selectivity. Second, we varied the water to ethanol ratio in carbon precursor mixtures for SWCNT growth. Using different characterization techniques, such as XRD and X-ray absorption spectroscopy, we monitored the changes of catalyst nanoparticles under different water contents to understand the effects of water on SWCNT purity and diameter selection.

- (2) Sulfur in various industrial feedstocks is generally regarded as a catalyst poison; however, controlled poisoning of metal catalysts by sulfur sometimes leads to improvement in both reactivity and selectivity (*Journal of Catalysis*, 1993, 142, 449-463). In some previous studies, small amount of sulfur was added in carbon precursors. Sulfur not only promoted the growth rate and the yield of carbon nanotubes but also strongly affects nanotube structures, such as shell number and diameter (*JACS*, 2011, 133, 5232–5235 and *Advanced Materials*, 2011, 23, 5064-5068). It is interesting to understand the role of sulfur in chiral selectivity growth. In this project, we introduced different sulfur-containing compounds into carbon precursors and studied the chirality selectivity change and carbon yield on a Co/SiO₂ catalyst.
- (3) TUD-1 has complex mesoporous structures, which make it challenging to elucidate the roles of different components in the catalyst. Thus, we prepared a model catalyst based on CoSO₄/SiO₂ by depositing cobalt (II) sulphate (the same metal species used in synthesizing Co-TUD-1) on commercially available high surface area silica gel. We found that this simple catalyst can also have selectivity towards (9,8) nanotubes, although the selectivity is lower than that of Co-TUD-1. Catalyst calcination was found to strongly affect the performance of this model catalyst. We optimized calcination conditions to understand what have been changed under different calcination conditions. Based on the findings, we further doped sulfur containing components into other Co catalysts to change their chirality selectivity in SWCNT growth.
- (4) We further used H₂S to sulfidize Co catalysts in an attempt to directly create active catalytic sites in order to achieve both good chirality selectivity and high carbon yield.
- (5) As-synthesized SWCNTs from CoSO₄/SiO₂ catalyst still contains significant amount of small-diameter nanotubes and large-diameter metallic nanotubes. For building high performance SWCNT based transistors, semiconducting nanotubes with narrow diameter distribution is desired. We used two approaches to further enrich (9,8) nanotubes. First, we used three fluorene based polymers with different side chain lengths and backbones to extract (9,8) nanotubes. Second, we explored a new aqueous two-phase separation method, which relies on the spontaneous redistribution of surfactant dispersed SWCNTs into two aqueous polymer phases with relatively different hydrophobicity.
- (6) Last, we used a silica capillary column as a linear hydrothermal microreactor to assemble nitrogen doped graphene oxide (GO) and SWCNTs into unique multiscale hierarchical structured hybrid fibers. We expected that such hybrid fibers would have both a large surface area and high conductivity for energy storage applications. Furthermore, the hydrothermal microreactor can be used as an effective platform, which enables controllable functionalization through a facile route to yield versatile carbon composite fibers with either capacitive or Faradic characteristics. We have explored nitrogen doping and incorporation of MnO₂ nanoparticles into hybrid fibers to build high energy density asymmetric micro-supercapacitors.

Results and Discussion:

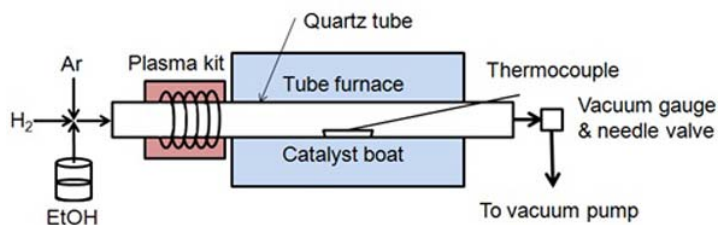


Figure 2. Schematic illustration of the remote plasma reactor developed in our lab.

SWCNTs with narrow chirality distribution can be synthesized using ethanol as carbon precursor by remote plasma enhanced chemical vapor deposition (see Figure 2). Use of remote plasma enables the decomposition of the nontoxic ethanol to occur away from the site of SWCNT growth. This allows separate manipulation of carbon radical generation and SWCNT growth. A series of syntheses were carried out at plasma power from 0 to 250 W and growth temperature from 625 to 875 °C. Our results have revealed that the plasma power and growth temperature affect carbon radical generation and recombination, as well as the reduction and nucleation of cobalt species. In addition, remote ethanol plasma etching does not damage the grown SWCNTs. The chirality of resulting SWCNTs shows minor changes under different plasma power. On the other hand, the diameter of SWCNTs can be adjusted (from 0.7 to 1 nm) by changing the growth temperature. At the optimum condition of 200 W plasma power and 775 °C growth temperature, (7,5) and (8,4), nanotubes account for more than 50% of all semiconducting nanotube species. These results demonstrate the potential of utilizing plasma process in chiral selective growth of SWCNTs.

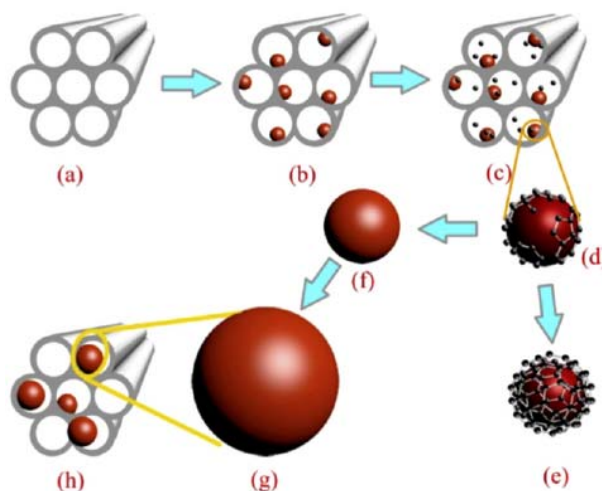


Figure 3. Schematic illustration of the effect of H_2O on catalyst particles in SWCNT growth.

We also synthesized SWCNTs using water assisted ethanol pyrolysis. The effect of varying the water to ethanol ratio in the reactant mixture was studied. The data from X-ray absorption spectroscopy indicate that with the addition of water, the cobalt metal particles were oxidized. X-ray diffraction analysis of CoC_x suggests that the formation of amorphous carbon on the surface of the Co particles was suppressed. Cobalt magnetization measurements were performed to study the size and anisotropy of cobalt particles. Thermogravimetric analysis data demonstrate

that with a water concentration of 7%, the yield increases by about 100% relative to pure ethanol synthesis. Raman and photoluminescence excitation spectroscopic data demonstrate that the SWCNT diameter increases (within the diameter range detected) with the water/ethanol ratio. From statistical SWCNT diameter distribution obtained from transmission electron microscopy, 65% of the SWCNT synthesized with 20% water in ethanol have diameters larger than 1.5 nm, but there is a severe decrease in yield and a modest decrease in selectivity of SWCNT. A mechanism of how the water influences the yield and diameter of SWCNTs is proposed as illustrated in Figure 3.

Co^{2+} ions are incorporated in the catalysts matrix (a). After hydrogen reduction, the cobalt ions are partially reduced by hydrogen, but remain anchored to the wall by interaction with cobalt catalysts and/or silica occlusion (b). When ethanol is introduced to the system, it decomposes and then produces methane and CO at the reaction temperature, which further reduces the cobalt ions into metallic cobalt (c). Carbon containing compounds may partially cover and dissolve in metallic cobalt and initiate SWCNT growth. During synthesis, some of the cobalt might be extensively covered by amorphous carbon (d). If sufficient amorphous carbon forms on the cobalt surface, the growth will stop (e). A right amount of water (<7%) can suppress the formation of amorphous carbon and revive the activity of cobalt catalysts (f). Thus improving the yield. At the same time, because the amorphous carbon may inhibit the cobalt particles from sintering, removing the amorphous layer might also encourage the sintering of the cobalt particles (g and h). A larger particle will initiate the growth of a larger-diameter SWCNT. When more water was added to the system (>7%), the yield decreased as a result of fewer cobalt particles available; excess water etching small-diameter SWCNT; and competing steam reforming reactions. However, the SWCNT diameter continues to increase.

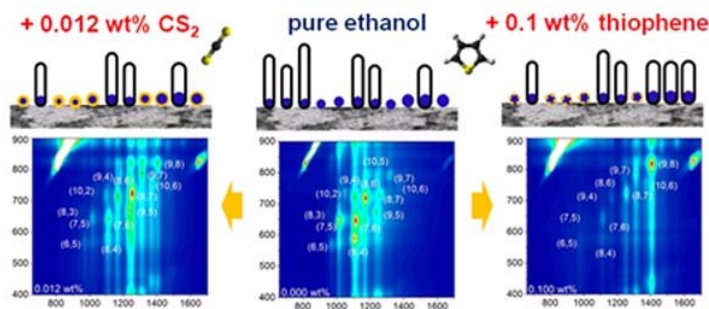


Figure 4. Schematic illustration of the effect of sulfur-containing compounds on SWCNT growth and photoluminescence maps of SWCNTs produced under different conditions.

We also demonstrated that introducing sulfur-containing compounds into carbon precursors may efficiently alter the chiral selectivity of a Co/SiO₂ catalyst toward different chiral species (see Figure 4). When carbon disulfide (0.0001 wt%) was added to ethanol, the carbon yield increased significantly from 4.8 to 14 wt% without chirality changes. Changes in chiral selectivity are correlated with the significant changes in the carbon yield. With further increase of carbon disulfide concentration, the chirality distribution shifted from smaller diameter chiral nanotubes, such as (7,6) at 0.9 nm, toward larger diameter chiral ones, such as (8,7) at 1 nm and (9,8) at 1.2 nm, in addition to a sharp decrease in the carbon yield. Further, when a different sulfur-containing compound was used, the chiral selectivity changed differently. Thiophene (0.1 wt%) in ethanol led to a good chiral selectivity toward (9,8) nanotubes with a relative abundance

of 43.1% among all semiconducting nanotubes. We propose that sulfur may selectively block active sites on Co particles through dynamic interactions among sulfur, hydrogen, carbon and Co metal particles. Our results suggest that sulfur-containing compounds may be used as an efficient additive to tune the chiral selectivity of catalysts in SWCNT synthesis.

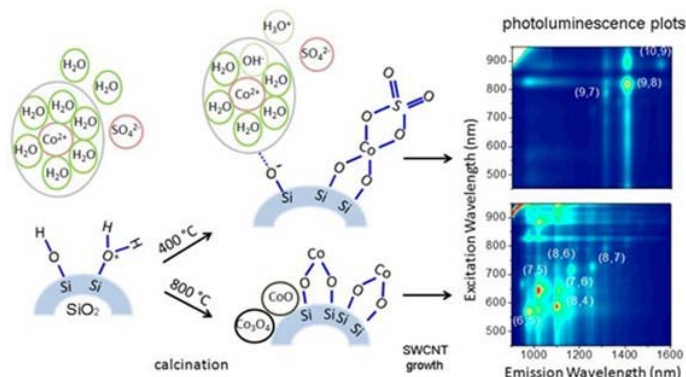


Figure 5. Schematic illustration of CoSO₄/SiO₂ catalyst at different calcination conditions and photoluminescence maps of SWCNTs produced under different calcination conditions.

CoSO₄/SiO₂ catalyst prepared by impregnating 1 wt% Co from Co (II) sulfate heptahydrate on fumed silica powder is an active catalyst for SWCNT growth. The catalyst shows unique selectivity toward the large-diameter single-chirality (9,8) nanotubes. When the catalyst is calcined in air at 400 °C, it yields 50.52% of (9,8) nanotubes among all semiconducting SWCNTs. The catalyst also possesses a passable carbon yield of 3.8 wt%, which is useful in developing a scalable SWCNT production process. Chiral selectivity of the catalyst is correlated with the catalyst calcination temperatures; the selectivity would shift to small-diameter nanotubes when the catalyst is calcined above 700 °C. The catalyst calcination plays a critical role in forming active Co species on SiO₂ surface for SWCNT growth. TEM, XRD, and physisorption results show that the chiral selectivity change is not resulted from the morphology or physical structure changes of the catalyst. H₂-TPR, UV-vis spectroscopy, and XAS studies demonstrate that, at low calcination temperature (<400 °C), Co ions adsorb on SiO₂ surface through electrostatic interaction and/or form strongly bonded Co to the SiO₂ surface through the oxolation reaction (see Figure 5). Sulfur exists as chelating bidentate SO₄²⁻ on the surface with Co atoms. The coexistence of S atoms near Co atoms may limit the aggregation of Co atoms or form various Co–S compounds, which may produce specific chiral selectivity toward the (9,8) nanotubes. With the increase in calcination temperature, some S atoms are removed from the catalyst, leading to the formation of surface Co oxides and Co silicates which are more selective to the small-diameter SWCNTs. We believe that novel sulfate-promoted catalysts may be further developed to improve the chirality control and the yield of SWCNTs, which eventually reveal their enormous potentials in electronic and optoelectronic applications.

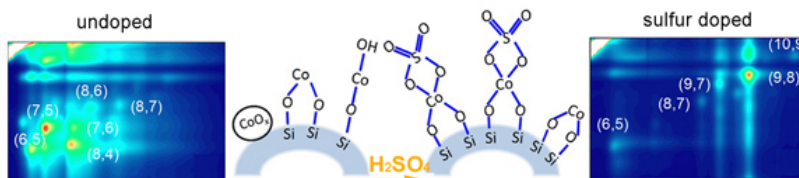


Figure 6. Schematic illustration of S doping on Co/SiO₂ catalyst and photoluminescence maps of SWCNTs produced under different conditions.

Based on the understanding of $\text{CoSO}_4/\text{SiO}_2$ catalyst, we showed that it is simple to convert three types of Co/SiO_2 catalysts, which are either inactive for the SWCNT growth or only selective to small-diameter nanotubes, into chirally selective catalysts to grow SWCNTs enriched with large-diameter (9,8) tubes (up to 40.5%) by doping catalysts with S (see Figure 6). We also proposed in the mechanism that S atoms near Co atoms assist the formation of Co nanoparticles which are selective to (9,8) tubes. Moreover, H^+ ions may react with CoO_x to form well dispersed Co hydrosilicate and surface Co silicate on SiO_2 , which increases the selectivity to SWCNTs. Our latest results suggest that direct sulfurization by H_2S could be even more efficient approach to creating active catalytic sites on Co catalysts. It will help to achieve both good chirality selectivity and high carbon yield. This work is still on-going.

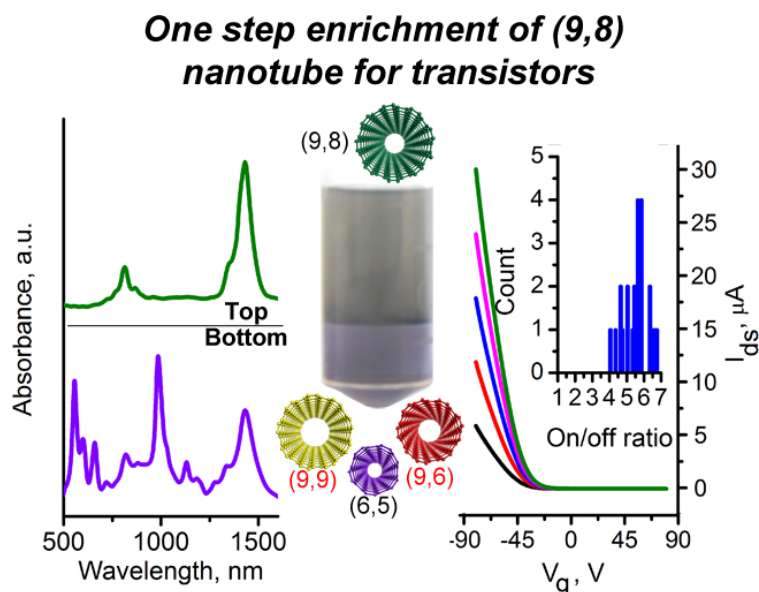


Figure 7. Schematic illustration of carbon nanotube separation in a two-phase separation method. Left shows the absorption spectra of separated nanotubes; and right shows transistors performance using separated nanotubes.

The (9,6) and (10,10) nanotubes are the major metallic species in as-synthesized SWCNTs from $\text{CoSO}_4/\text{SiO}_2$ catalyst. For potential applications, it is desirable to further increase the purity of (9,8) nanotubes, as well as to remove metallic species. We found that a solution of poly[(9,9-dihexylfluorenyl-2,7-diyl)-co-(9,10-anthracene)] (PFH-A)/toluene (0.75 mg/mL) can selectively extract semiconducting nanotubes with 78.3% (9,8) and 12.2% (9,7) among all semiconducting species. In contrast, other fluorene-based polymers (poly(9,9-dioctylfluorenyl-2,7-diyl), PFO and poly(9,9-din-octylfluorenyl-2,7-diyl), POF) show poorer selectivity. Furthermore, molecular dynamic simulations show that the (9,8) selectivity by PFH-A depends on the bending and alignment of its alkyl chains and the twisting of its two aromatic units (biphenyl and anthracene). The strong π - π interactions between polymers and SWCNTs help to increase the extraction yield, but it is not beneficial for chiral selectivity. It is important to consider the matching between the curvature of SWCNTs and the flexibility of the polymer side chain and aromatic backbone units to design novel polymers for selective extraction. More recently, we further demonstrated simultaneous diameter and metallicity enrichment of large-diameter (9,8) nanotubes in one separation step from as-synthesized SWCNTs on $\text{CoSO}_4/\text{SiO}_2$ catalyst using the new aqueous two phase separation method (see

Figure 7). Systematic separation parameter studies showed that the optimum separation conditions are (1) sodium dodecyl sulfate / sodium cholate surfactant ratio of 7/9, (2) addition of KSCN concentration of 10 mM, and (3) separation temperature of 5 °C. Under this optimum separation conditions, the abundance of (9,8) nanotubes in the top layer increases to 84.1%, and the ratio of semiconducting to metallic increases more than 40 times compared to as-synthesized nanotubes. The enriched (9,8) nanotubes were used to fabricate thin-film transistors with high on/off ratio (up to 10^7) and good mobilities (up to $5 \text{ cm}^2/\text{Vs}$), demonstrating the great potential of using these (9,8)-enriched nanotubes for transistor applications. Furthermore, the (9,8)-enriched nanotubes with a narrow emission window around 1400 nm may be useful for many applications in the new generation of optoelectronic devices.

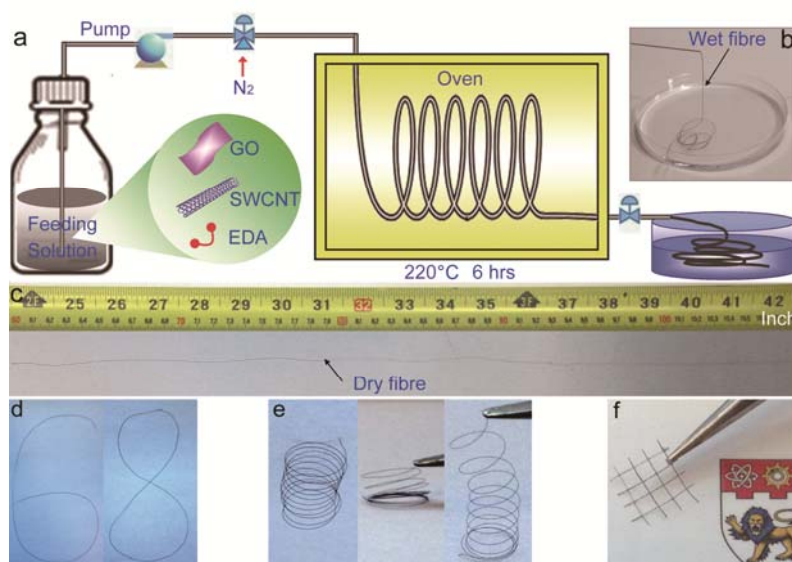


Figure 8. Schematic of the synthesis of carbon hybrid microfibers.

Using a silica capillary column as a linear hydrothermal microreactor, we have developed a scalable method to continuously produce carbon microfibres with hierarchical structures comprising nitrogen-doped reduced GO (rGO) and acid-oxidized SWCNTs. Directed assembly of these two carbon components within the microfibre confinement in the presence of ethylenediamine led to the formation of three dimensional pillared assemblies along the fiber length. The resultant hybrid fiber exhibits high packing density and large ion-accessible surface area, as is desirable for high-volumetric-performance micro-supercapacitors. The fiber has a conductivity of 102 S/cm and a specific surface area of $396 \text{ m}^2/\text{g}$. We have shown that the capacitor electrodes fabricated from these fibers have a specific volumetric capacity of 305 F/cm^3 in H_2SO_4 (at 73.5 mA/cm^2 , in a three-electrode cell) and 300 F/cm^3 in polyvinyl alcohol(PVA)/ H_3PO_4 (at 26.7 mA/cm^2 , in a two-electrode cell). An all-solid-state micro-supercapacitor made from two such parallel fiber electrodes on a flexible polymeric substrate, using PVA/ H_3PO_4 as the gelled electrolyte, without binder, current collector, separator or any other packaging material, exhibited a long cycle life (93% device capacitance retention over 10,000 cycles) and an ultra high volumetric energy density of 6.3 mWh/cm^3 , about tenfold higher than those of state-of-the-art commercial supercapacitors and even comparable to the $4 \text{ V}/500 \text{ mAh}$ thin-film lithium battery. The micro-supercapacitor delivers a maximum power density of up to $1,085 \text{ mW/cm}^2$, a value comparable to that of typical commercially available supercapacitors and more than two orders higher than the power density of lithium thin-film

batteries. The micro-supercapacitors can be integrated either in series or in parallel to meet the energy and power needs in various potential applications, including portable flexible optoelectronics, multifunctional textiles, sensors and energy devices, as exemplified in this study by powering a TiO₂-based ultraviolet photodetector and a light-emitting diode. Such device could bridge the energy density gap between microbatteries and micro-supercapacitors for miniaturized portable electronics. The synthetic methodology we have developed is scalable and the resultant hierarchically structured fibers could be regarded as a general architecture for designing functional hybrid microfibres. **This work published on Nature Nanotechnology has been downloaded more than 13000 times worldwide since its publication in 2014, and has also attracted a great deal of media attentions, including more than 100 websites such as the Register, CNN Money, Yahoo News, IEEE spectrum, eurekaalert, sciencedaily et al.. Other research articles have cited it 49 times in 6 months (Google Scholar).**

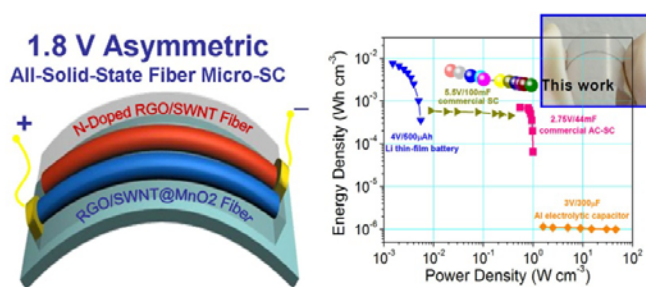


Figure 8. Schematic of asymmetric fiber supercapacitors based on hybrid carbon fibers, and their energy and power density.

From this synthesis platform, we further demonstrated the synthesis and controllable functionalization of rGO/SWCNT all-carbon fibers, yielding versatile fibers with either capacitive or Faradic characteristics for designing high-performance asymmetric fiber micro-supercapacitors. The capacitive-type nitrogen-doped rGO/SWCNT fibers obtained through *in situ* nitrogen-doping with urea in the flexible capillary column show tunable specific capacitances from 1.75 to 2.37 mF/cm, while the Faradic-type fibers created by redox deposition of MnO₂ on the rGO/SWCNT fibers have specific capacitances ranging from 1.76 to 3.30 mF/cm. Both types of functionalized fibers outperform the pristine rGO/SWCNT fibers (1.5 mF/cm), while retaining fiber geometry and mechanical flexibility. By matching the specific capacitances of one MnO₂-coated rGO/SWCNT fiber as battery-type (positive) electrode and the other N-doped rGO/SWCNT fiber as capacitor-type (negative) electrode to achieve the charge balance between two fiber electrodes, we designed and constructed the fiber-based solid-state asymmetric micro-supercapacitors with polymer gelled neutral electrolyte on a flexible polymer substrate. The optimized device exhibits a stable and high voltage window of 1.8 V and excellent cycling stability (87% capacitance retention after 10,000 cycles), as well as good flexibility. More importantly, the device delivers a high volumetric energy density of ~5 mWh/cm³, superior to most reported solid-state micro-supercapacitors to date and even comparable to the 4V/500-μAh thin-film lithium battery, while its power density of 929 mW/cm³ is comparable to typical commercially activated carbon supercapacitors and about two orders higher than that of thin film lithium batteries. This facile design and rational synthesis open an avenue to fabricate high-performance fibrous micro-scale energy storage devices and our developed fiber-based asymmetric micro-supercapacitor with high operation voltage and remarkable volumetric energy

density have great potentials in flexible and portable electronics, as exemplified by powering a ZnO based UV photodetector in this study. Furthermore, the applications of the newly-developed various composite fibers are not limited to advanced electrode materials for micro-supercapacitors, they have much broader potentials for functional textile, smart cloths, flexible electronics, sensors, as well as biofuel cells.

List of Publications and Significant Collaborations that resulted from your AOARD supported project: In standard format showing authors, title, journal, issue, pages, and date, for each category list the following:

a) Papers published in peer-reviewed journals,

1. Yuan, Y; Wei, L; Jiang, W; Goh, K; Lau, R; **Chen, Y***; Sulfur induced chirality changes in single-walled carbon nanotube synthesis by ethanol chemical vapor deposition on Co/SiO₂ catalyst, *Journal of Materials Chemistry A*, **2015**, 3, 3310–3319
2. Wang, H; Yuan, Y; Wei, L; Goh, K; Yu, DS; **Chen, Y***; Catalysts for Chirality Selective Synthesis of Single-Walled Carbon Nanotubes, *Carbon*, **2015**, 81, 1-19
3. Yu, DS; Goh, K; Zhang, Q; Wei, L; Wang, H; Jiang, W; **Chen, Y***; Controlled Functionalization of Carbonaceous Fibers for Asymmetric Solid-State Micro-Supercapacitors with High Volumetric Energy Density, *Advanced Materials*, **2014**, 26, 6790-6797
4. Si, R; Wei, L; Wang, H; Su, D; Mushrif, S; **Chen, Y***; Extraction of (9,8) Single-Walled Carbon Nanotubes by Fluorene-Based Polymers, *Chemistry - An Asian Journal*, **2014**, 9, 868–877
5. Yu, DS; Goh, K; Wang, H; Wei, L; Jiang, W; Zhang, Q; Dai, L; **Chen, Y***; Scalable synthesis of hierarchically-structured carbon nanotube-graphene fibres for capacitive energy storage, *Nature Nanotechnology*, **2014**, 9, 555–562
6. Wei, L; Bai, SH; Peng, WK; Yuan, Y; Si, RM; Goh, KL; Jiang, RR; **Chen, Y***; Narrow-chirality distributed single-walled carbon nanotube synthesis by remote plasma enhanced ethanol deposition on cobalt incorporated MCM-41 catalyst, *Carbon*, **2014**, 66, 134-143
7. Ren, F; Kanaan, S; Majewska, M; Keskar, G; Azoz, S; Wang, H; Wang, X; Haller, G; **Chen, Y**; Pfefferle, L; Increase in the Yield of (and Selective Synthesis of Large-diameter) Single-Walled Carbon Nanotubes through Water-assisted Ethanol Pyrolysis, *Journal of Catalysis*, **2014**, 309, 419–427
8. Wang, H; Fang, R; Liu, C; Si, R; Yu, D; Pfefferle, L; Haller, G; **Chen, Y***; CoSO₄/SiO₂ Catalyst for Selective Synthesis of (9,8) Single Walled Carbon Nanotubes: Effect of Catalyst Calcination, *Journal of Catalysis*, **2013**, 300, 91–101
9. Wang, H; Goh, K; Xue, R; Yu, D; Jiang, W; Lau, R; **Chen, Y***; Sulfur Doped Co/SiO₂ Catalysts for Chirally Selective Synthesis of Single Walled Carbon Nanotubes, *Chemical Communications*, **2013**, 49, 2031 – 2033

b) Conference presentations,

1. **Chen, Y***; Novel Catalyst for the Chirality Selective Synthesis of Single Walled Carbon

Nanotubes, USA Air Force Office of Scientific Research, Organic materials chemistry program review meeting, Washington DC, USA, October 2014

2. **Chen, Y***; Yu, D; Scalable Synthesis of Hierarchically-Structured Carbon Nanotube-Graphene Fibres for Capacitive Energy Storage, 14th International Conference on the Science & Application of Nanotubes, Los Angeles, USA, June 2014
3. **Chen, Y***; Selective Synthesis and Enrichment of (9,8) Single-Walled Carbon Nanotubes for Macroelectronics, The 2nd Carbon Nanotube Thin Film Electronics and Applications; Los Angeles; USA, June 2014 (**Invited Talk**)

c) Manuscripts submitted but not yet published

1. Wei, L; Liu, B; Wang, X; Gui, H; Yuan, Y; Ng, A.K.; Zhou, C; **Chen, Y***; Enrichment of Large-Diameter (9,8) Single Walled Carbon Nanotubes via Aqueous Two-Phase Separation and Their Thin Film Transistor Applications, *Advanced Electronic Materials*, **2015**, under review

d) Interactions with industry or with Air Force Research Laboratory scientists or significant collaborations that resulted from this work

1. I visited AFRL on 12 Nov 2013, hosted by Dr. Benji Maruyama. I gave a research seminar on chiral selective synthesis of single walled carbon nanotubes to researchers, and had meetings with AFRL researchers and discussed various research topics.
2. Attended Organic Materials Chemistry Portfolio Review meeting in DC, Oct 2014
3. New cooperation with Dr. Seung Min Kim (Korea Institute of Science and Technology), who is recently funded by AROAD, on TEM analysis of metal catalyst particles after SWCNT synthesis.
4. Cooperation with Prof. Chongwu Zhou, who is recently funded by Air Force on chirality selective growth of SWCNTs. Our cooperation research result has been submitted for publication on *Advanced Electronic Materials*.
5. Cooperation with Prof. Ralph Krupke from Karlsruhe Institute of Technology. We have recently received a grant on "Selective synthesis and enrichment of single-chirality carbon nanotubes for device applications" funded by Singaporean-German Researcher Mobility Scheme.